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Design and Evaluation of PM Ti Surfaces Modified by Colloidal Techniques and Diffusion Processes for Biomedical Applications

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The aim of this work was the modification of the composition and surface microstructure of powder metallurgy titanium to improve the wear resistance and reduce the elastic modulus while maintaining the corrosion behavior, characteristics needed for biomedical applications. For this purpose, Mo and Nb coatings were produced by colloidal techniques. Stable aqueous suspensions were prepared from micro-sized powder of Mo and Nb particles, deposited onto the powder metallurgy titanium substrates (green or sintered). After a heat treatment to promote the diffusion and the consolidation of the layers, microstructural changes were obtained. In the case of green substrates, the co-sintering process provides a diffusion depth of 85-100 micron. In the as-sintered case, a uniform depth of 40-65 microns was reached. The surfaces were characterised by micro-hardness, corrosion and tribocorrosion testing, and the results showed that hardened surfaces presented lower tendency to corrosion both under static conditions and under sliding.

KEYWORDS: Titanium, Surface treatments, Mo, Nb, Diffusion, Colloidal techniques, Powder Technology, Tribocorrosion.

1. *Introduction*

It is well known that properties such as corrosion and wear resistance are very important for metallic biomaterials in orthopaedic applications [1], [2]. Titanium and its alloys offer an excellent combination of mechanical properties, high corrosion resistance and suitable biocompatibility aspects, but unfortunately also exhibit poor wear and tribological behaviour [3], [4].
In terms of metallic implants, not only corrosion and wear processes take place separately but also in a simultaneous way which is known as tribocorrosion phenomena. Tribocorrosion is an irreversible process having a particular importance for biomaterials being subjected to the combined action of corrosion and wear [5], [6]. That results in a great concern because it can lead to an acceleration of material loss and the release of metallic ions; inducing the release of osteolytic cytokines affecting harmfully the mechanical integrity of implants [7]. On the other hand, prosthetic implants also need of low Young's modulus to reduce the stress shielding effect which leads to death of bone cells due to their higher stiffness than that of bone [1], [8]. Implant failure is highly influenced by the surface properties of the employed biomaterial. Thus, surface engineering play a vital role and numerous surface treatments are explored to enhance hardness, Young's modulus, wear resistance and tribological properties of titanium alloys [9], [10].

The present study aimed to get a first approach to the corrosion and tribocorrosion behaviour of Ti-Mo and Ti-Nb surface modified materials in comparison with bared titanium in 9 g/l NaCl solution. The objective was to have a better knowledge about the effect created by the Mo or Nb introduction on green and sintered powder metallurgy titanium substrates, comparing the (40-100 μm) bi-phasic diffusion layers originated by co-sintering (in green Ti substrates) or diffusion (in sintered Ti substrates) processes in terms of microstructural features, hardness and tribocorrosion behaviour.

2. *Experimental section*

2.1 Preparation of the surface modified Ti-based materials

Powder metallurgy (PM) surface modified Ti-Mo and Ti-Nb alloys were produced. Prior to the surface modification, titanium substrates were processed from hydride-dehydride (HDH) commercially pure titanium powder (CPTi grade 4) (GfE Metalle und Materialien GmbH, Germany) with particle size below 75 μm. Green (as-pressed) and sintered substrates were fabricated following a route established in previous works. Green substrates were prepared by uniaxial pressing at 600 MPa employing a cylindrical mold of 16 mm in diameter where the walls were lubricated with zinc stearate. For the sintered substrates, after the pressing step, a sintering cycle was performed in high vacuum (10^{-5} mbar) at 1250 ºC for two hours with a heating and cooling rate of 5 ºC/min. Pieces were placed inside the furnace in a bed of zirconia balls as a support. Density of the samples before and after sintering was measured geometrically to know the total porosity of the material. Green compacts shown values of 84% of the theoretical and the sintered ones, 95%.

Green titanium samples did not need any surface preparation before the surface modification (molybdenum or niobium deposition). However, the sintered ones were prepared as follow: grinding on sandpaper from 180 to 1000 grade, rinsing in distilled water, ultrasonic cleaning in ethanol and drying with hot air.

Surface modification was carried out from micro-sized Mo and Nb powders, with 1-2 μm and 44 μm in size, respectively. First, an aqueous suspension containing 10% volume Mo particles was deposited by spraying. On the other hand, a suspension of Nb particles 1.5 M was prepared in acetone and deposited by immersion. Both surface modifications took place onto green and sintered titanium substrates. After, a thermal treatment was applied for the co-sintering-diffusion or only diffusion of the coatings. The cycle was performed under high vacuum (10^{-5} mbar), heating at 5 ºC·min^{-1} to 1100 ºC with a dwell time of 3 hours and cooling down at 5 ºC·min^{-1}.
Final surfaces were finished by a soft grinding step on sandpaper of 1000 grade to remove the rests of no diffused coating and polishing down to 0.3 μm using alumina suspensions. With purpose of comparison, a polished sintered titanium substrate was chosen as a control sample. Figure 1 summarizes the followed routes, samples designation and the nomenclature followed further on.

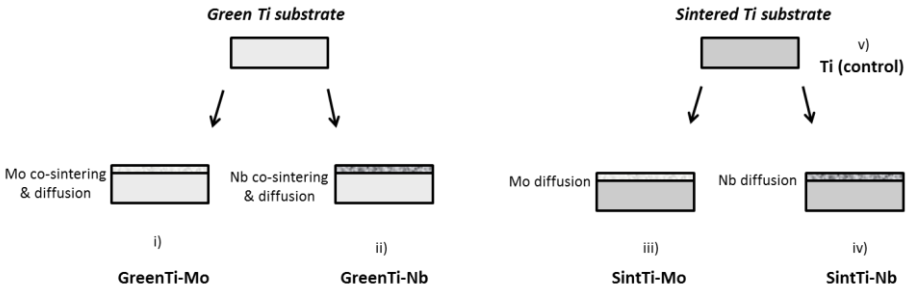

Figure 1. Scheme of the surface modified titanium samples

2.2 Preparation of the designed materials for surface and microstructural characterization

Designed materials were prepared for characterization in two ways. On one hand, cross-section was prepared in order to see the microstructural changes. On the other hand, the surfaces of designed materials were prepared to remove the possible loose particles and to flatten the surfaces for a correct measurement by grinding with sandpaper of 1000 grade and polishing down to 0.3 μm alumina suspension.
Regarding to the cross-section, the microstructural analysis was carried out by field emission-scanning electron microscopy (FE-SEM FEI, Teneo) and composition profiles were taken with EDAX, energy dispersive X-ray spectroscopy (EDS).
As far as the surface characterization is concerned, measurement of roughness and hardness was performed. The roughness was analysed by Hommel tester T500 profilometer, and Vickers micro-hardness by Zwick Roell micro-hardness tester with a diamond tip and load of 100 g (0.1HV) and a ZHμ HD hardness testing software data analyzer. Finally, the corrosion and tribocorrosion behavior was tested on these surfaces.

2.3 Corrosion tests

Corrosion tests were performed on the modified materials, being evaluated by electrochemical impedance spectroscopy (EIS). An electrolyte of 9 g/l NaCl at room temperature was used as a first approach, and because it represents the major compound of Hank´s Balanced Salt Solution and Phosphate Buffered Saline physiological solutions. Impedance measurements were carried out using an Autolab Potentiostat PGSTAT302N and the impedance spectra were acquired in the frequency range from 10 mHz to 10 kHz by applying input sinusoidal signals of ±10 mV. A three-electrode electrochemical cell was used which included a platinum wire as counter electrode, an Ag/AgCl (KCl 3M) as reference electrode and the titanium alloy sample under study as working electrode with an exposed area of 0.28 cm^2. Electrode potentials at open circuit were registered versus the Ag/AgCl (KCl 3M) reference electrode whose relative potential to the standard hydrogen electrode (SHE) exhibits a value of 205 mV. In order to verify the reproducibility of the measurements, three repetitions of every test were realized.

2.4 Tribocorrosion tests

Tribocorrosion measurements were carried out in an electrochemical cell placed on a ball-on-plate-tribometer (CETR-UMT-2) where the working surface of the sample (which was the moving body) was placed facing upwards against the static counter material (10 mm diameter alumina ball, Ceratec). Electrochemical measurements were realized in 9 g/l NaCl solution at room temperature using Voltalab PGZ 100 potentiostat. A two electrode set up was used where a saturated calomel electrode (SCE) was used as the reference electrode and the samples, having an exposed area of 177 mm^2, were used as the working electrode. Open circuit potential (OCP) was measured before, during and after sliding, taking the sliding action place once the values of OCP were stable in each test (1 h approximately). The established parameters for the tests were: 1 N as the normal load, 1 Hz of frequency, 10 mm of total stroke length and 1800 s as the sliding time.

3. Results and discussion

3.1 Microstructure and physical properties

Microstructure of the surface modified samples is shown in Figure 2. As it can be seen, a gradient of composition was obtained by the molybdenum (Figure 2a-b) and niobium (Figure 2c-d) diffusion. The diffusion areas obtained are formed by colonies of α + β; being that two phase region of different thickness depending on the initial state of the titanium substrate (green or sintered). Mo and Nb surface modification performed on green substrate (Figure 2a, c) shows a diffusion layer depth of 85 and 100 μm, respectively. Figure (2b, d) present the surface modification reached in sintered substrate. In the last case, the diffusion area is narrower but with more homogenous and uniform aspect; presenting a depth of 45 μm for the Ti-Mo sample and 65 μm for the Ti-Nb. A concentration profile of Nb in green titanium substrate is shown in Figure 2e, as an example of the concentration variation of the diffusing element as a function of the distance from surface, obtained from EDS analysis on the cross-section of Figure 2c. The peaks and valleys seen in this graph correspond to the β (Nb-rich) and α layers of the colonies, which become bigger inwards.

After preparation of surfaces by grinding and a final polishing step, the tested materials present the following roughness average values (Ra (μm)): 0.11 ± 0.1 (Ti control), 0.20 ± 0.4 (GreenTi-Mo), 0.45 ± 0.1 (SintTi-Mo), 0.16 ± 0.3 (GreenTi-Nb) and 0.39 ± 0.4 (SintTi-Nb).

According to micro-hardness (0.1HV) tests, the following values were obtained from the hardened surfaces with the surface modification: 370 ± 17 (GreenTi-Mo), 430 ± 21 (SintTi-Mo), 295 ± 16 (GreenTi-Nb) and 315 ± 14 (SintTi-Nb); exhibiting all of them significantly higher values than that of the Ti control, 279 ± 10. These values are the average of 5 measurements. The results of Ref. [11] show similar micro-hardness values, although other report some higher values [12], [13].

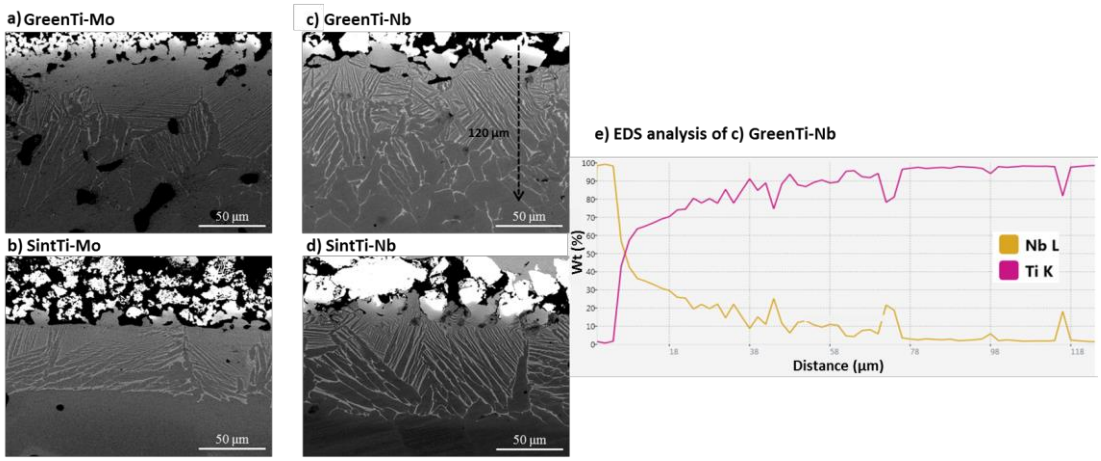

Figure 2. Cross-sectional SEM micrographs of the diffusion areas for the surface modified materials: a) GreenTi-Mo, b) SintTi-Mo, c) GreenTi-Nb and d) SintTi-Nb. e) EDS analysis of the variation in Nb content as a function of the distance from surface

3.2 Corrosion behaviour

Figure 3 presents the Nyquist (Figure 3a) and Bode (Figure 3b) plots for the four modified materials and the control sample. From Nyquist plot, it can be observed a larger arc for the SintTi-Mo and SintTi-Nb in comparison with the Ti control sample and the GreenTi-Mo and GreenTi-Nb. It can be resulted in better corrosion behaviour because of the higher polarization resistance, which means that a successful surface modification has been carried out. However, it has been found no superior corrosion resistance response from the surface modified green titanium samples, probably due to the higher amount of porosity, as it can be appreciated in the upper SEM micrographs of Figure 2. Bode plots show the impedance modulus, |Z|, that is almost the same for the modified and the control samples, values between 10^5 - 10^6 Ω, only a slightly difference is clear in the case of the GreenTi-Nb sample whose |Z| is of one magnitude order less. As the EIS measurements have been performed at time zero of exposition to the electrolyte, the high value of |Z| reached suggests that no significant deterioration occurred in the homogeneous and compact barrier formed in the diffusion layer.

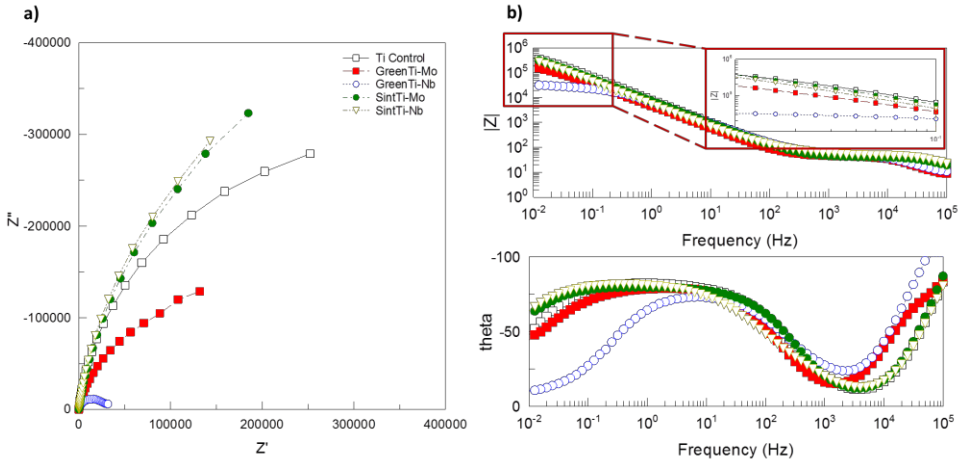

Figure 3. a) Nyquist and b) Bode plots obtained for the modified surfaces and control samples in 9 g/l NaCl solution

3.3 Tribocorrosion behaviour

The evolution of the open circuit potential (OCP) before, during, and after sliding together with the coefficient of friction (COF) during sliding is given in Figure 4. As it can be seen, OCP values were stable for all the materials before sliding, and when sliding starts a sudden decrease of OCP was perceived, that is an expected behaviour for passive metals due to the damage suffered on the passive films formed [14]. Nevertheless, similar to the stabilization values, all modified surfaces presented more positive potential values under sliding, as compared to the titanium control sample.

After sliding, potential values increased up to near the initial ones for almost all the materials; being that increase more pronounced for the case of the modified materials with niobium content, GreenTi-Nb and SintTi-Nb. On the other hand, as far as the coefficient of friction is concerned, similar COF values have been obtained for the materials with niobium and the titanium control sample, although for those with molybdenum a slightly increase on the COF values during sliding has been detected.

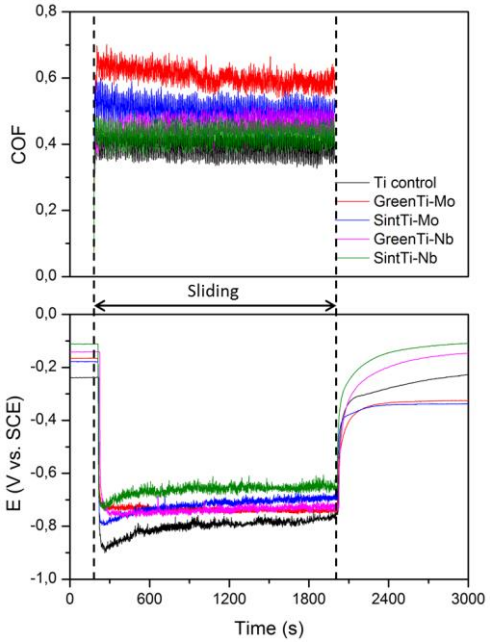

Figure 4. Evolution of the OCP together with COF values during sliding

4. Conclusions

Powder metallurgy (PM) Ti-Mo and Ti-Nb surface modified samples were processed by colloidal techniques and diffusion processes. The surface modification study has been successfully carried out onto green (as-pressed) and sintered titanium, generating diffusion layers; deeper (85-100 μm) in the green substrates and narrower (45-65 μm) but more homogeneous in the sintered ones. As a first insight on this study, the corrosion and tribocorrosion behaviour of the modified materials have been investigated. EIS studies have displayed better corrosion resistance for the SintTi-Mo and SintTi-Nb materials, although the modification onto green substrates showed a slightly lower corrosion resistance. In the tribocorrosion experiments, the COF values were similar or little superior to the value presented by the titanium control; however all the modified surface materials exhibited less negative corrosion potentials than the unmodified titanium; pointing out lower tendency to corrosion.

Acknowledgments

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